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Process for the preparation of urea granules

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PROCESS FOR THE PREPARATION OF UREA GRANULES

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For the production of urea granules various methods are known. In the past prilling was the predominant method, wherein a substantially anhydrous urea melt is sprayed from the top of a prilling column in a rising stream of air of ambient temperature in which the droplets solidify to form so-called prills. These prills have a relatively small maximum diameter and are mechanically rather weak.

10

Urea granules having larger dimensions and better mechanical properties are presently being produced by the granulation of a substantially anhydrous urea melt or of an aqueous urea solution in a fluidized bed, such as, for instance, described in

15 US-4.619.843.

In this patent publication a process is described for the preparation of granules in a fluidized bed process, by feeding a urea melt to a fluidized bed of solid urea nuclei, upon which the nuclei grow by solidification of the urea melt on the nuclei. The process is not only suitable for the preparation of urea granules, but also to the granulation of other materials such as sulphur and ammonium nitrate. In the fluidized bed feeding devices are used comprising a central channel from where the liquid material is supplied as a virtually closed, conical film and a channel concentric therewith through which a gas stream is supplied. The main advantage of this process is that it is low in energy consumption.

20

The urea melt that is delivered to the fluidized bed comprises, apart from urea, also water. The presence of water has some very important advantages. First, concentration of the urea melt in an evaporator before feeding it to the fluidized bed is simpler and less energy consuming when some water is left present in the urea melt. Second, the evaporation of the water in the fluidized bed improves the heat balance resulting into less fluidizing air needed for cooling. As a result thereof a smaller scrubbing section is needed to clean the fluidizing air.

25

30

The main disadvantage of the presence of water in the urea melt is the high concentration of granulation additives that needs to be present in the urea melt to be able to form urea granules out of the melt in a fluid-bed granulator.

35 Granulation additives are expensive and hazardous for health and environment.

Examples of granulation additives used during urea granulation are formaldehyde, methylolurea, formurea and hexamethylenetetramine. The granulation additives are

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added to reduce dust formation during granulation, to obtain urea granules with adequate mechanical properties and to obtain free-flowing urea granules.

The present invention is based on extensive investigations aiming at the reduction of the concentration of granulation additives during granulation, while at the same time the mechanical properties, such as the crushing strength and the caking tendency, and the free-flowing properties of the granules are maintained or even improved. Also reduction of dust formation was aimed at.

It has now been surprisingly discovered that when in the urea melt that is delivered to the fluid-bed the weight ratio biuret/water is 0.25 to 10 the concentration of granulation additives that must be used can be greatly reduced. Granulation additives can even be absent during granulation.

Biuret is an organic by-product that can be obtained during urea production, which has no disadvantageous effects on health and environment. During preparation of the urea granules the weight ratio biuret/water in the urea melt is 0.25 to 10, preferably 0.3 to 7 and most preferably 0.3 to 3.

The weight ratio biuret/water in the urea melt can be obtained by a large number of different methods. Examples of these methods are given hereafter. The weight ratio biuret/water can be obtained in and/or downstream of an evaporator that is placed upstream of the feeding device. All kinds of commercially available evaporators can be used; for instance VOP-type evaporators. Also, between the evaporator and the feeding device water or a biuret-rich stream can be delivered to the urea melt to obtain the weight ratio biuret/water.

The weight ratio biuret/water can also be obtained in a vessel that is present between the evaporator and the feeding device. Biuret can be obtained in the urea melt when the temperature of the melt is higher than 130 °C. The vessel can be kept at a temperature above 130 °C and the residence time of the urea melt can be chosen in such a way that a urea melt is obtained with a weight ratio biuret/water that is 0.25 to 10.

The weight ratio biuret/water of the urea melt between the evaporator and the feeding device can also be obtained in other ways. For instance, by heating the piping to feed the urea melt to the feeding device.

Preferably, the weight ratio biuret/water in the urea melt is obtained by using two subsequent evaporators wherein part of the urea melt leaving the first evaporator is fed to the second evaporator and wherein a part of the urea melt leaving the first evaporator is combined with the urea melt leaving the second evaporator. This

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has the advantage that the ratio biuret/water can be changed easily by variation of the part of urea melt that flows from the first evaporator to the second evaporator.

The feeding device delivers the urea melt in the form of a film to a fluidized bed of solid urea nuclei, upon which the nuclei grow by solidification of the urea melt on the nuclei. It is necessary that the urea melt is delivered to the fluidized bed in the form of a film to prevent dust formation. In principle the film can have all kinds of configurations, but a virtually closed conical film is preferred.

The urea melt is introduced into the fluidized bed of nuclei from the bottom upwards with the aid of at least one feeding device provided with a central channel through which the urea melt is supplied and a channel concentric therewith through which a gas stream is supplied with a linear upward velocity higher than that of the fluidization gas. The gas stream creates a rarefied zone in the bed above the feeding device. The urea melt after exiting the central channel enters the rarefied zone. Before hitting the film, the gas stream sucks nuclei from the bed, entrains them and is thereby slowed down, so that both the film and the gas stream upon impact are deflected, and the entrained nuclei penetrate the film and are thereby moistened with a small amount of urea melt, which subsequently, in the rarefied zone, can solidify to such an extent that after exiting the rarefied zone the particles are sufficiently dry to prevent agglomeration.

A closed conical film can, in principle, be obtained in various ways. For example, the urea melt can with the aid of a tapered part at the end of the outlet channel be converted to a film. Preferably, the conical film is obtained by giving the urea melt a rotation. Of course, besides the rotational speed given to the material, also the hydrostatic pressure on the urea melt is important. In general, the urea melt is supplied under a hydrostatic pressure of 0.15 to 0.60 MPa, in particular 0.20 to 0.40 MPa. By preference, a feeding device provided with a rotation chamber is used.

It has been found to be advantageous that the surface of the film has hardly any ripples, since then a uniform distribution of the urea melt over the passed-through nuclei is obtained. This is influenced by, among other things, providing the outlet part of the feeding device with a smooth wall. In addition, care should be taken that the urea melt in the film has not too high an internal turbulence. It has been found that for obtaining a sufficiently smooth film the dimensionless Weber number ( $We\delta$ ), expressed as

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$$We_{\delta} = \frac{\rho_L U_L^2 \delta}{\sigma_L}$$

where:

- 5  $\rho_L$  is the density of the urea melt, in kilograms per cubic metre,  
 $U_L$  is the potential velocity of the urea melt, in metres per second,  
 $\sigma_L$  is the surface tension of the urea melt, in Newtons per metre, and  
 $\delta$  is the film thickness upon exit from the central channel, in metres,  
 should be smaller than 2500, in particular smaller than 2000. It has been found that to  
 10 this end the melt velocity should in general be at most 30 m/sec and preferably 10-25  
 m/sec.

The gas stream takes up nuclei and is thereby slowed down before  
 hitting the film. This is preferably achieved by making the gas channel lead into the  
 fluidized bed in a lower place than the central channel. In this way, the gas stream can  
 15 entrain nuclei along some distance and give them a certain velocity before they hit the  
 film. This so-called free distance can vary within wide limits, for example 0.5-5.0 cm.  
 Preferably, a free distance of 1-4 cm is used.

In the present process, as the gas stream preferably air is used,  
 which is supplied with a velocity of at least 50 m/sec, in particular 50-400 m/sec., in  
 20 general under a feed pressure of 0.11 to 0.74 MPa. The temperature of this gas stream  
 can differ. In general, a gas stream is used with a temperature about equal to that of  
 the urea melt. The required amount of this gas stream is in the present invention  
 exceptionally low. In general, a weight ratio of gas to urea melt of between 0.1 and 0.8,  
 in particular between 0.2 and 0.6 is applied.

25 After exiting from the gas channel, the gas stream sucks nuclei from  
 the bed and entrains them. The velocity of the gas stream thereby decreases, while the  
 nuclei acquire a certain velocity, for example 0.5-5 m/sec. Upon impact with the film,  
 the velocity of the gas stream has decreased to such an extent that the impulse of the  
 gas and the impulse of the film are about equal. By impulse is meant here the product  
 30 of mass flow rate and velocity. If upon impact the impulse of the film is too high  
 compared to that of the gas stream, the gas stream is strongly deflected outwards  
 resulting in disturbance of the rarefied zone. On the other hand, if upon impact the  
 impulse of the gas stream is too high compared to that of the film, the film is forced  
 inwards to such an extent that a considerable number of nuclei will no longer contact

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the urea melt and will therefore no longer be moistened. Upon impact, both the film and the gas stream are slightly deflected and virtually no gas-melt mixing takes place. The extent to which the film is deflected inwards and the extent to which the gas stream is deflected outwards are determined by the above-mentioned impulses and, to a lesser extent, by the angle at which impact occurs. This angle is determined by the vertex angle of the film, and the angle at which the gas stream possibly converges. It has been found that after exiting from the gas channel the gas stream by itself slightly converges in the bed, so that in the majority of cases it is not necessary to apply a converging gas channel. Possibly, at the outlet opening the gas stream is made to converge under an angle of 5-25°, in particular 5-10°. In general, the angle of impact will be 50 to 85°, in particular 60-70°.

When the film and the gas stream make impact, the nuclei entrained in the gas stream on account of their mass fly almost straight ahead, that is, through the film. These nuclei are thereby moistened with a thin layer of urea melt, which completely or almost completely solidifies in the rarefied zone. The amount of urea melt taken up depends on, among other things, the film thickness and the particle diameter. The film thickness upon impact is generally 50-250  $\mu\text{m}$ . The particle diameter may vary within wide limits, depending on the composition of the melt, the size of the nuclei introduced into the bed, and the number of times such a nucleus has already been moistened.

The gas stream does not only transport particles but also serves to create the rarefied zone above the feeding device. This zone should be of sufficient height to allow the urea melt on the particles to solidify to a sufficient extent, for example about 30 cm, but on the other hand it should be prevented, in view of dust emission, that the surface of the bed is locally broken. These conditions are determined by the mass and the velocity of the gas stream and the height of the bed, which is, for example, 40-100 cm.

For granulation the width of the gas stream upon exit from the gas channel is also relevant. In the case of a very wide gas zone, it is found that on the outer side of the gas stream a number of particles are carried along which are not moistened by the film. In general the width of the gas stream is chosen between 0.25 and 4 times the average diameter of the nuclei.

As nuclei in the fluidized bed, in principle all kinds of pellets can be used, for example prills separately prepared from a portion of the urea melt to be

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sprayed, or from a melt obtained by melting of the oversize fraction obtained after screening of the granulate. Preferably, as nuclei, granules are used which have been obtained during screening and/or crushing a small portion of of the granulate obtained from the bed. The average diameter of these nuclei may vary, partly depending on the  
5 nature of the material to be granulated and especially on the desired particle size of the product. Also the quantity of nuclei introduced may vary.

The bed of nuclei is kept in a fluidized state by an upward-flowing gas, in particular air. This fluidization gas should have a minimum superficial velocity to ensure that the bed is completely kept in a fluidized state. On the other hand, this  
10 velocity should be as low as possible, in connection with energy costs and to prevent dust emission. In general, a fluidization gas with a superficial velocity of 1.5-3.5 m/sec., more in particular 1.8-3.0 m/sec. is used. The temperature of the fluidization gas may vary, partly depending on the desired bed temperature, which, as usual, is set by a convenient choice of the temperature of the material to be sprayed, the spraying gas,  
15 the nuclei supplied and the fluidization gas.

The invention will be explained in detail with reference to the accompanying figures.

In Figure 1 to 5 some different processes for the preparation of urea granules according to the invention are shown.

20 In Figure 1 U represents the urea process wherein the urea melt is obtained. In this urea melt the weight ratio biuret/water is 0.015.

The urea melt is led to the evaporator (E) to obtain the weight ratio biuret/water according to the invention, which is 0.5. After the evaporator the urea melt is led to the spraying devices (S) in the granulator (G). In the spraying devices the urea  
25 melt is sprayed together with the air stream (A). Also fluidisation air is fed to the granulator.

In figure 2 a process for the preparation of urea granules is presented according to figure 1. To the first evaporator a urea melt is led with a weight ratio biuret/water 0.014. The urea melt that leaves the first evaporator has a weight ratio  
30 biuret/water of 0.1 and is for 75% led to the second evaporator. After the second evaporator the weight ratio biuret/water is 3.33. This stream of urea melt is combined with the the rest of the urea melt leaving the first evaporator giving a urea melt with a weight ratio biuret/water of 0.45 that is led to the spraying devices.

In figure 3 a process for the preparation of urea granules is presented  
35 according to figure 1 wherein after the evaporator a vessel (V) is placed for further



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treatment of the urea melt. The weight ratio biuret/water in the urea melt that enters the evaporator is  $3 \cdot 10^{-4}$ . After the evaporator the weight ratio biuret/water is 0.05. In the vessel the urea melt is kept for 10 minutes at a temperature of 135 °C and is then led to the spraying devices. The weight ratio biuret/water in the urea melt that is sprayed is .

5 2.5.

In figure 4 a process for the preparation of urea granules is presented according to figure 1 wherein after the evaporator a heating device (H) is placed for further treatment of the urea melt. The weight ratio biuret/water in the urea melt that enters the evaporator is  $3 \cdot 10^{-4}$ . After the evaporator the weight ratio biuret/water is 0.05. In the heating device the urea melt is kept for 1 minute at a temperature of 150 °C and is then led to the spraying devices. The weight ratio biuret/water in the urea melt that is sprayed is 2.5.

In figure 5 a process for the preparation of urea granules is presented according to figure 1 wherein after the evaporator a heating device (H) and a cooler (C) are placed for further treatment of the urea melt. The weight ratio biuret/water in the urea melt that enters the evaporator is  $3 \cdot 10^{-4}$ . After the evaporator the weight ratio biuret/water is 0.05. In the heating device the urea melt is kept for 30 seconds at a temperature of 160 °C and is then led to the cooler. In the cooler the urea melt is kept for 10 seconds at a temperature of 135 °C and is then led to the spraying devices. The weight ratio biuret/water in the urea melt that is sprayed is 2.0.

#### Examples

The mechanical properties of the granulate produced in the granulator are characterized by a number of quality parameters.

25 One such quality parameter is the crushing strength of a granule, defined as the pressure at which a granule crushes into fine particles. The crushing strength of a granule is of importance in the handling and storage of the urea product between the manufacturers plant and the end user. In order to assure that also at the end-user the product confirms user expectations (such as easy handling, good spread ability, low/no losses in the application) the crushing strength of the granulate as produced in the manufacturers plant should be more then 2 MPa, end preferably more then 3 MPa. It has now been found that the crushing strength of the produced granulate can be influenced by the biuret/water ratio in the urea melt that is used in the urea melt feed to the granulator. A high biuret to water ratio improves the crushing strenght to such an

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extent that granulate with a good crushing strength can be obtained with considerably lower, or even no, dosing of the above-mentioned granulation additives.

Example A:

- 5 A fluid bed granulator, applying a feeding device that delivers the urea melt in the form of a virtually closed conical film, with a We number of 1500 was used in a process set up as given in Fig 1. A urea melt having a biuret/water ratio of 0.6 was supplied to this feeding device. Without dosing any formaldehyde, the crushing strength of the produced urea granules had an acceptable value of 2.3 MPa. After
- 10 dosing of 0.2% of formaldehyde (relative to the total amount of melt supplied to the feeding device), the crushing strength of the urea granules increased to 3.2 MPa.

Comparative Experiment 1:

- 15 According to the same process as described under Example A urea granules were prepared.

- By changing the process parameters in evaporator E, a urea melt with a biuret/water ratio of 0.15 was supplied to the feeding device. 0.5% of formaldehyde (relative to the total melt supply to the feeding device) was added via dosing device D1. Urea granules with a crushing strength of 2.8 MPa were obtained.
- 20 When the dosing of formaldehyde was stopped, the crushing strength of the urea granules dropped to the unacceptable low value of 1.7 MPa.

- Another important mechanical property of the produced granulate is its caking tendency. A non-caking, free flowing product is of importance to assure easy
- 25 handling and minimum spillage of the product during transport, as well as at its final application. The most common final application of urea is fertilizer. In most countries, nowadays fertilizer is spread over the land by rolling mechanical devices. It is very important that in these mechanical devices the urea is free flowing and is without lumps. Lumps, or non-free flowing behavior of the urea granulate would result in
- 30 uneven distribution of the fertilizer over the land, with a negative influence on the crop-yield in those land area's where a lower than average dosing of fertilizer is applied. The caking tendency of urea can, for example, be measured in a test, where a sample of the granulate is stored for a certain time under a specified pressure. The pressure that is required to break the sample after this storage is a measure for the
- 35 caking tendency of the granulate. The higher this breaking pressure, the higher the

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caking tendency of the product. In general, the caking tendency should be lower than 0.8 bar in order to ensure that the application of the fertilizer at the end-user will be trouble free.

It is well known that the caking tendency of urea granulate can be reduced by the addition of granulation additives. It is also known that the caking tendency of urea granulate can be reduced by covering the surface of the granulate with surface-active components. For this purpose sometimes aqueous solutions of a saponifier (such as alkyl sulphonate or alkyl sulphate) are sprayed over the surface of the urea granulate. A disadvantage of these kind of surface protection to the granulate is the high cost of these additives.

It has now been found that the caking tendency of urea granulate can also be influenced by the biuret/water ratio of the melt to the feeding device of the granulator. By choosing the right biuret/water ratio in this feedstream, a granular product with good to excellent non-caking behavior can be obtained without, or with greatly reduced dosing of abovementioned additives.

#### Comparative Experiment 2:

A fluid bed granulator, applying a feeding device that delivers the urea melt in the form of a virtually closed conical film, with a We number of 1200 was used in a process set up as given in Fig 1. A urea melt having a biuret/water ratio of 0.1 was supplied to this feeding device. 0.5% of formaldehyde (relative to the total melt supply to the feeding device) was added via dosing device D1. 0.1% (relative to the total melt supplied to the feeding device) of an aqueous solution of ethyl-hexyl sulfate was added to the granulate via dosing device D3. Urea granules with an excellent non-caking behavior were obtained (caking tendency < 0.1 bar). When the dosing of formaldehyde and of ethyl-hexyl sulphate was stopped, the caking tendency of the urea granules appeared to be fully unacceptable (caking tendency 2 bar).

#### Example 2:

The evaporation section between the urea plant and the feeding device to the granulator was modified in the way as illustrated in Fig 2 (E2 was added, E1 representing the original evaporator E from figure 1). With this modified feeding arrangement a urea melt with a biuret/water ratio of 3.0 could be obtained. Applying the same feeding device as before, the caking tendency of the urea granules improved to an acceptable value (0.4 bar). After dosing only 0.05% of the same aqueous solution of

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ethyl-hexyl sulphate, the caking tendency of the urea granules returned to its original excellent value of <0.1 bar. In this way the handling of the toxic formaldehyde solution could be avoided, whilst the cost of the expensive ethyl-hexyl sulphate dosing was halved.

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CLAIMS

1. Process for the preparation of urea granules in a fluid-bed granulator, by using at least one feeding device to deliver a urea melt in the form of a film to a fluidized bed of solid urea nuclei, upon which the nuclei grow by solidification of the urea melt on the nuclei, characterised in that in the urea melt that is delivered to the fluid-bed the weight ratio biuret/water is 0.25 to 10.
2. Process according to claim 1, characterised in that the weight ratio biuret/water is 0.3 to 7.
3. Process according to claim 1, characterised in that the weight ratio biuret/water is 0.3 to 3.
4. Process according to any one of claims 1-3, characterised in that the weight ratio biuret/water in the urea melt is obtained in and/or downstream of an evaporator.
5. Process according to any one of claims 1-4, characterised in that the weight ratio biuret/water in the urea melt is obtained by using two subsequent evaporators wherein part of the urea melt leaving the first evaporator is fed to the second evaporator and wherein a part of the urea melt leaving the first evaporator is combined with the urea melt leaving the second evaporator.
6. Process according to any one of claims 1-5, characterised in that water is delivered to the urea melt between the evaporator and the feeding device to obtain the weight ratio biuret/water in the urea melt.
7. Process according to any one of claims 1-6, characterised in that a biuret-rich stream is added between the evaporator and the feeding device to obtain the weight ratio biuret/water in the urea melt.
8. Process according to any one of claims 1-7, characterised in that a vessel is present between the evaporator and the feeding device wherein the weight ratio biuret/water in the urea melt is obtained.
9. Process according to any one of claims 1-8, characterised in that the temperature of the urea melt is raised between the evaporator and the feeding device to obtain the weight ratio biuret/water in the urea melt.
10. Process according to any one of claims 1-9, characterised in that the urea melt is delivered to the fluidized bed in the form of a virtually closed conical film.
11. Process according to any one of claims 1-10, characterised in that the feeding

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devices comprise a central conduit for delivering the urea melt to the fluid-bed and a conduit concentric with the central conduit through which a gas stream is delivered.

- 5      12. Process according to any one of claims 1-11, characterised in that the velocity of the urea melt when exiting the central channel of the feeding device is between 10 to 25 m/s.
13. Process according to any one of claims 1-12, characterised in that the urea melt is delivered to the fluid-bed in a higher place than the gas stream.
- 10      14. Process according to any one of claims 1-13, characterised in that the gas stream is applied with a velocity of 50-400 m/s, under a feed pressure of 0.11-0.74 MPa.
15. Process according to any one of claims 1-14, characterised in that the weight ratio of the gas stream to the urea melt is 0.2-0.6.

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**ABSTRACT**

Process for the preparation of urea granules in a fluid-bed granulator,  
by using at least one feeding device to deliver a urea melt in the form of a film to a  
5 fluidized bed of solid urea nuclei, upon which the nuclei grow by solidification of the  
urea melt on the nuclei, characterised in that in the urea melt that is delivered to the  
fluid-bed the weight ratio biuret/water is 0.25 to 10.

- 1/3 -

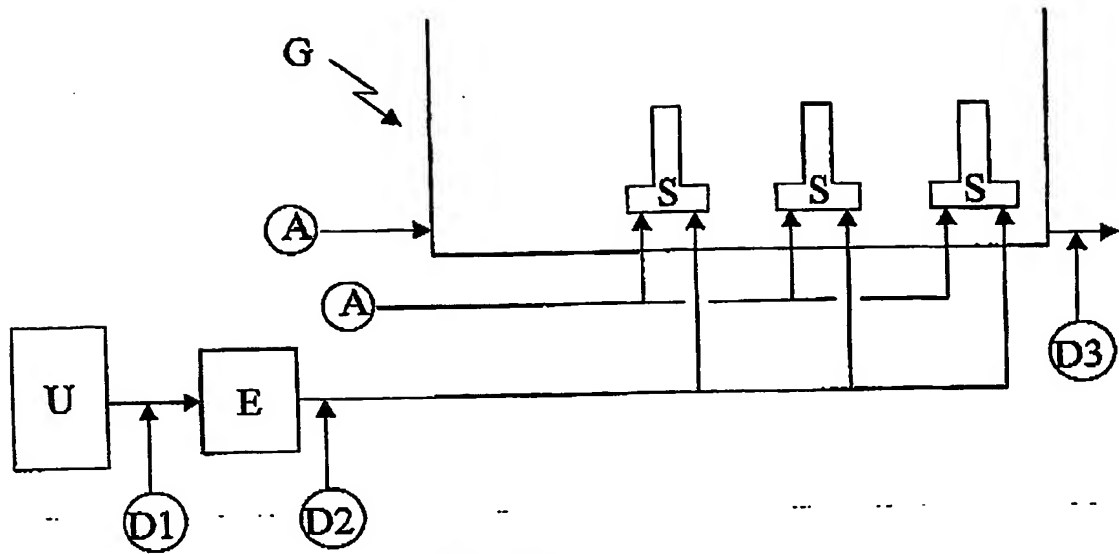


Figure 1/5

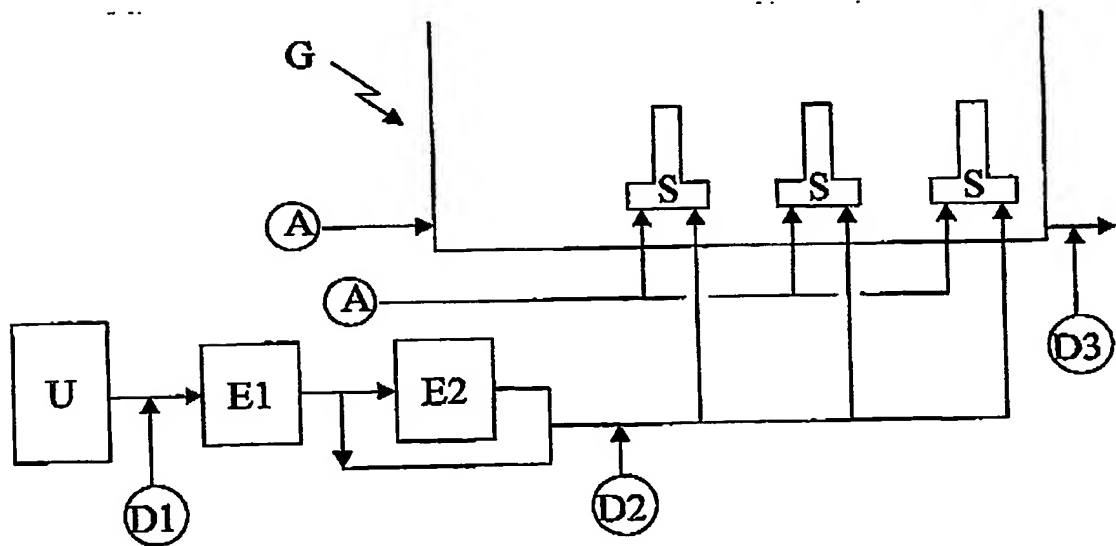


Figure 2/5



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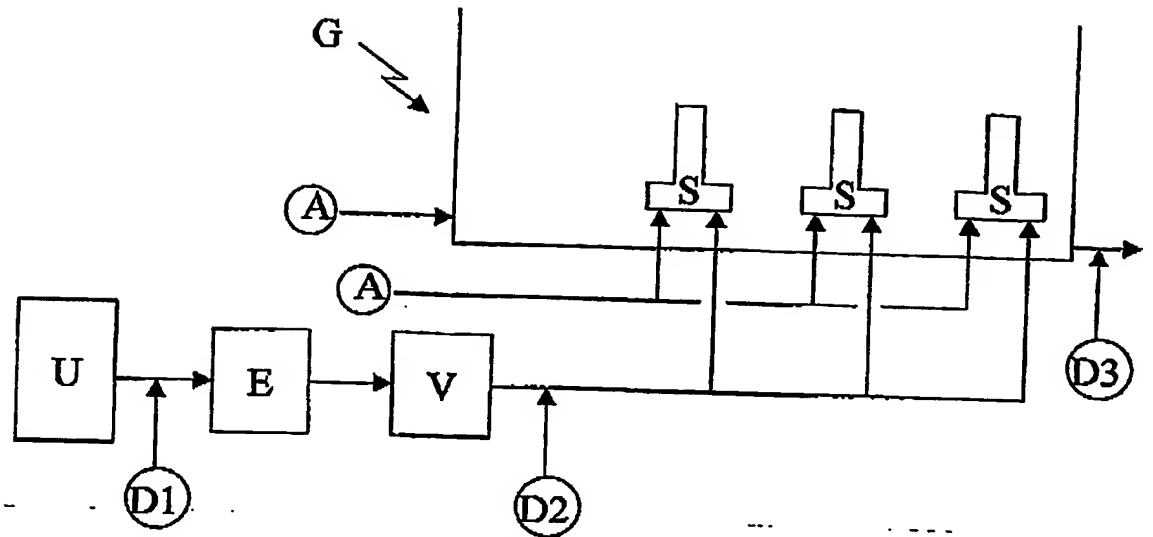


Figure 3/5

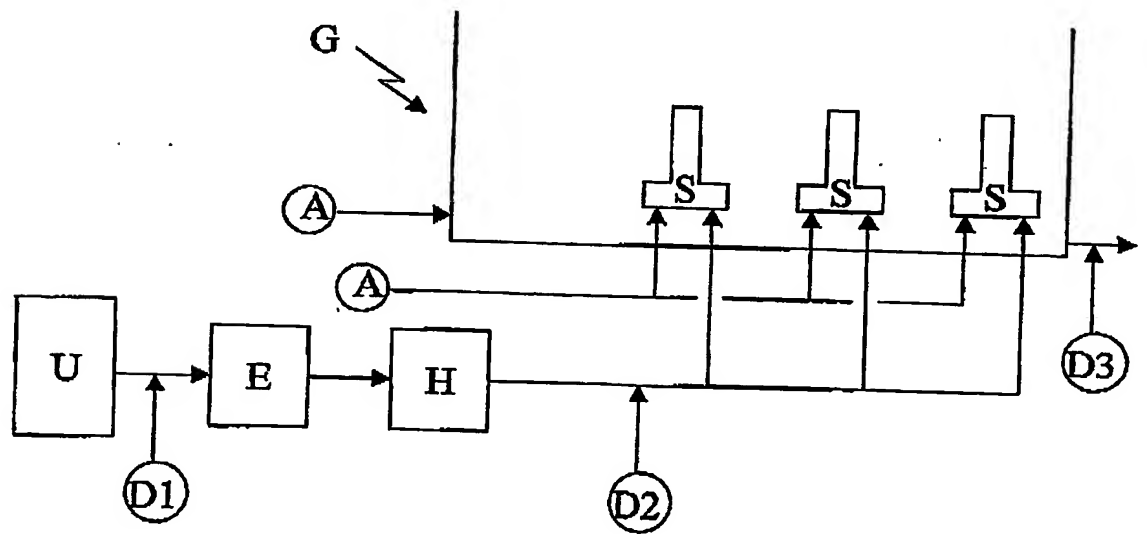
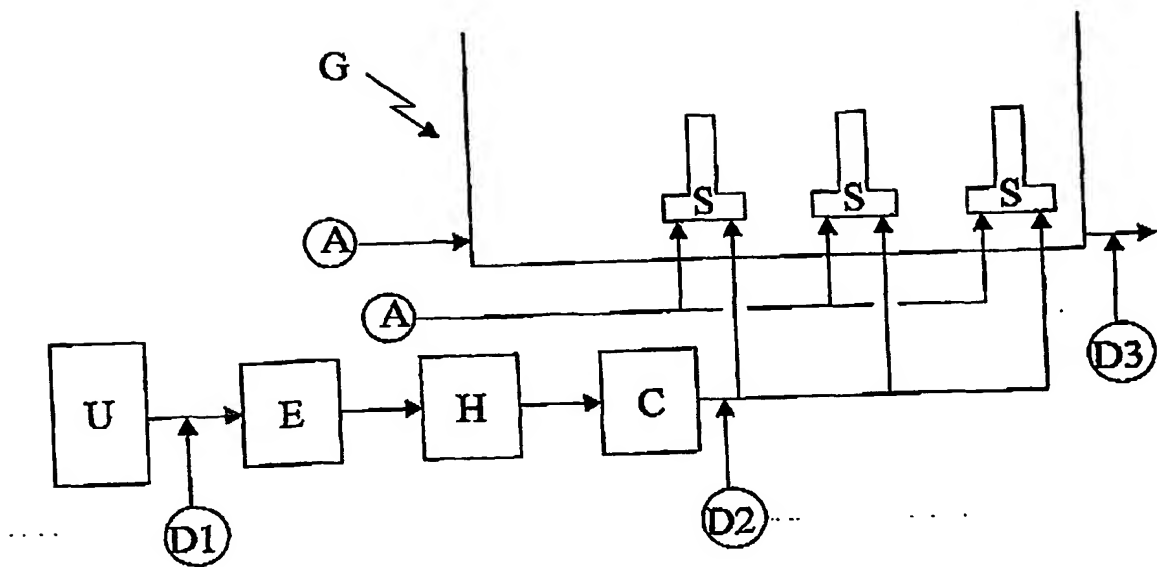


Figure 4/5

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Figure 5/5

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